

## Silica Coating of Nanoparticles by the Sonogel Process

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A modified aqueous sol–gel route was developed using ultrasonic power for the silica coating of indium tin oxide (ITO) nanoparticles. In this approach, organosilane with an amino functional group was first used to cover the surface of as-received nanoparticles. Subsequent silica coating was initiated and sustained under power ultrasound irradiation in an aqueous mixture of surface-treated particles and epoxy silane. This process resulted in a thin but homogeneous coverage of silica on the particle surface. Particles coated with a layer of silica show better dispersability in aqueous and organic media compared with the untreated powder. Samples were characterized by high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and the zeta potential.

### Introduction

Coating nanoparticles with different materials to form encapsulated or core–shell structures has attracted lots of attention over many years because of novel properties such as biocompatible surfaces and improved physical and chemical properties that can be introduced for a broad range of applications.<sup>1–3</sup> The core particles can be unidimensional, such as spherical nanoparticles,<sup>4,5</sup> or elongated objects such as nanorods,<sup>6</sup> nanofibers,<sup>7</sup> or nanotubes<sup>8</sup> and can be composed of metal,<sup>2,9,10</sup> semiconductor,<sup>11</sup> polymer,<sup>12</sup> or biocompatible materials.<sup>13</sup> There are numerous coating procedures that are widely used, including direct precipitation of coating materials onto the nanoparticles,<sup>12,14</sup> graft polymerization,<sup>15</sup> and microemulsion. However, when it comes to the coating of more complex-shaped particles on the nanometer scale, the sol–gel process, which can be carried out in solution, provides many advantages. Nanoparticle coating via the sol–gel process is generally performed using metal alkoxide precursor molecules and preformed particles through direct surface reactions utilizing specific functional groups on the particle's surface to induce coating. Among the precursors, silicon alkoxide has been extensively investigated not only because silica layers offer the possibility to produce nanocomposites with tailored physical properties<sup>16,17</sup> but also because such relatively inert coatings

may be applied in order to protect nanoparticles from potential degradation in their application environment.<sup>2,9,18–20</sup> Well-established flexible silicon chemistry also opens the door to further surface treatment of the coated nanoparticles for advanced applications such as bimolecular attachment, which can be used to deliver specific ligands to target sites via antibody–antigen recognition.<sup>21</sup>

However, all published methods are preferably applied only to particles that are stably dispersed throughout the coating process. A fundamental problem often encountered in real nanoparticle applications is that it is generally very hard to keep dispersions of nanoparticles stable. Such problems are more severe when nanopowders are dispersed in solution because hard aggregates are generally formed during powder synthesis, which require higher-energy input to break them apart. Techniques such as media milling and high shear homogenization have been used commercially for deaggregation and emulsification whereas power ultrasound has been proven to be an ideal option for this purpose. Power ultrasound is a cheap method of generating cavitation for emulsification, and it is relatively easy to scale up. Under irradiation using powerful ultrasonic waves, large particles or particle aggregates can be fragmented into smaller particles because of the combined effect of impact (jet) milling, attrition milling, knife milling, and direct pressure milling brought about by ultrasonic cavitation.<sup>22</sup> Such effects will reduce the particle size and thus increase reactivity in solution.<sup>23</sup>

Power ultrasound also promotes high-energy chemical reaction through the process of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid.<sup>24</sup> In the early 1980s, Tarasevich described an approach to sol–gel processing by exposing tetraethoxysilane (TEOS)–water mixtures to intense ultrasonic irradiation.<sup>25</sup> Zarzycki's and Esquivias' groups con-

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ducted extensive research to establish the practical consequences of this approach on the kinetic and textural characteristics of the so-called sonogels<sup>26</sup> thereby produced. Reviews have been published<sup>27,28</sup> that cover the diverse techniques employed to investigate microstructural evolution during different steps in the sonogel process and some applications for the sonogels that were produced. During the sonogel process, hydrolysis proceeds by exposing the initial mixture (alkoxide + acidified water) to ultrasonic waves in an open glass container. The energy dose delivered to the sonogel system is set by varying the output powder of the generator, with treatment time providing an additional parameter for controlling the sol and gel properties.<sup>29</sup>

In this work, we have developed a two-step sonogel surface treatment process to coat silica onto commercially available nanopowders. An advantageous feature of the process is that it combines the beneficial effects of power ultrasound on both the dispersal of the nanopowders and on initiating sol–gel reaction, thereby modifying the particle's surface with a layer of silica. Hard aggregation problems during the redispersal of nanopowders are commonly observed, and improvement in the dispersability of the particles was realized as a result of this coating process.

### Experimental Section

**Nanopowder.** Indium tin oxide (ITO) powder was purchased from Inframat Advanced Materials. The claimed mean particle size is 40 nm, and the specific area is 40 m<sup>2</sup>/g.

**Chemical Reagents.** *N*-Aminoethyl-3-aminopropyltrimethoxysilane (AEAPS) with a brand name of Dynasylan DAMO and 3-glycidyloxypropyltrimethoxysilane (GPTS) with a brand name of Dynasylan GLYMO were purchased from Degussa, GmbH.

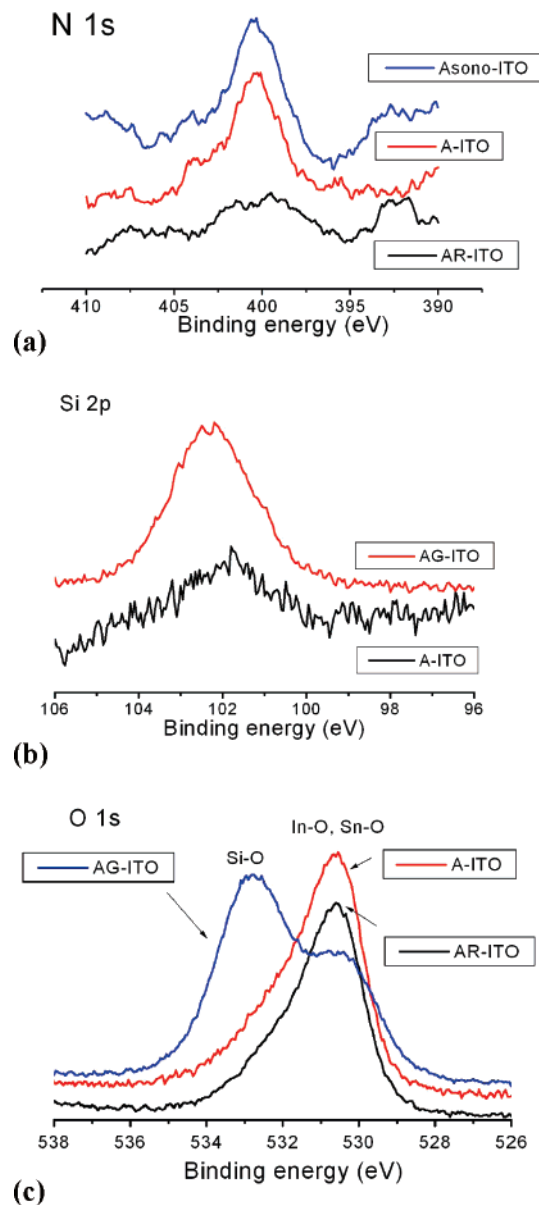
**Ultrasonicator.** A Fisher (model 550) sonicator was purchased from Fisher Scientific (SEA) Pte. Ltd.

**Chemical Process. Aminosilane Surface Treatment.** A typical treatment process is as follows: 2 g of as-received ITO powder was added to 20 g of deionized water acidified by acetic acid while stirring vigorously. AEAPS (8 mL) was slowly added to the dispersion while stirring, and the mixture was refluxed for 12 h. Upon completion of the treatment, ITO particles were separated by centrifuging and were washed three times each with water and ethanol.

**Silica Coating under Ultrasound Irradiation.** A typical process for this step is as follows: 10 g of GPTS was mixed slowly with 20 g of water acidified by hydrochloric acid (HCl) (pH 1.5). The aforementioned aminosilane-treated powder (4 g) was then added to the mixture, contained in a 100 mL glass bottle. The bottle was then placed under the probe of the sonicator for continuous ultrasound irradiation with the output power set to 60 W or above. The sol–gel reaction was initiated after approximately 2 to 3 min of ultrasound irradiation, upon which white foam was generated by the release of alcohol upon extensive hydrolysis of GLYMO. Sonication was applied for 20 min, after which the solution was stirred for several more hours. Once the reaction was completed, the particles were gathered by centrifuging and were washed repeatedly with water and then either dried for characterization or kept dispersed in water or organic solvents.

Samples were named AR-ITO (as-received sample), A-ITO (aminosilane-treated), AG-ITO (aminosilane-treated powder with a silica coating through the sonogel process), and Asono-ITO (aminosilane-treated powder sonicated in acidified water).

**Sample Characterization.** X-ray photoelectron spectroscopy (XPS) was carried using an ESCALAB 250 manufactured by Thermo



**Figure 1.** XPS spectra of (a) N 1s, (b) Si 2p, and (c) O 1s of powder samples.

VG Scientific. The scanning condition for each energy range was saved and applied to all other samples for consistency. Powder samples were observed by a Philips 300M high-resolution transmission electron microscope (HRTEM) operated at 300 kV. The zeta potential measurement was carried out using a Marvin Zetasizer (Nano Series) connected to an MPT2 multipurpose titrator. HCl (0.1 N) and NaOH (0.02 and 0.1 N) were used as titrants.

### Results and Discussion

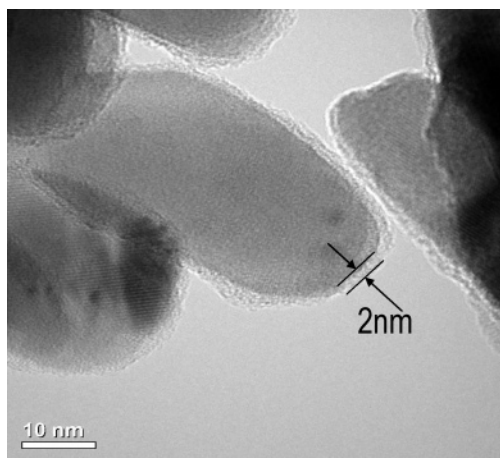
XPS was used to verify the functional groups present on the surfaces of particles at different stages of the process. XPS spectra of N 1s, O 1s, and Si 2p in all samples are displayed in Figure 1a–c. As shown in Figure 1a, there was no N 1s found in the AR-ITO whereas the appearance of a small peak at 400 eV for the A-ITO sample is attributed to nitrogen in the amino groups of AEAPS, which can be used to prove the presence of grafted aminosilane after the first step. No peak around 102 eV was found in AR-ITO sample, confirming the absence of silica in the as-received powder. There was a relatively small amount of silicon found in A-ITO (shown in Figure 1b), and a significant increase was observed for AG-ITO, corresponding to the silica coated

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**Figure 2.** TEM of AG-ITO.

onto the surface of nanoparticles after the two-step sonogel process. Figure 1c shows the binding energy for O 1s for all three types of samples. Two significantly different binding states can be found here: the peak at 530 eV corresponds to O–In and O–Sn in the as-received powder, and the shoulder at higher energy corresponds to O–Si in the coated layer.<sup>30</sup> Meanwhile, another shift toward higher energy at just below 1000 eV was also found (not shown here). This can be assigned to the Auger line of oxygen KL<sub>1</sub>L<sub>23</sub>, KL<sub>23</sub>L<sub>23</sub> and supports the existence of new oxidation states on the sample surface.

The harsh conditions generated when cavitation collapse occurs under the influence of power ultrasound waves may lead to the production of excited states to bond breaking.<sup>31</sup> There is thus a concern that ultrasound irradiation in the sonogel coating step may potentially remove or degrade the amino functional groups grafted onto the ITO surface in the previous surface-modification step. To test this theory, a separate experiment was conducted in which A-ITO was simply sonicated in a mixture of acidified water/ethanol under the same ultrasound conditions as used for the silica coating step but without epoxy silane, the powder that was gathered for XPS characterization with the sample name Asono-ITO. As shown in Figure 1a, nitrogen remained on the particle surface after sonication because there is no significant change between the A-ITO and A-sonoITO at N 1s. Hence it is clear that the grafted amino groups were robust enough to react with epoxy silane in the subsequent sonogel process.

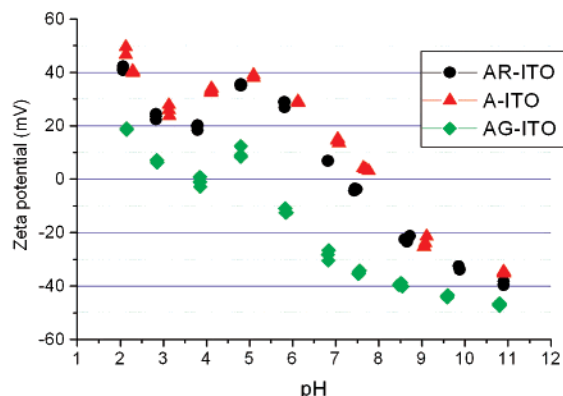
Figure 2 shows a representative TEM micrograph of an AG-ITO sample. A uniform, high-quality silica coating on the AG-ITO particles can be observed to have formed as a product of the two-step surface treatment. The coating thickness is between 1.5 and 2.5 nm.

Surface modification of oxide particles generally results in a change in the pH dependence of the zeta potential in aqueous dispersions. Zeta potentials of AR-ITO, A-ITO, and AG-ITO in the pH range from 2 to 11 are shown in Figure 3. For AR-ITO, the isoelectric point (IEP) is at pH 7–8. At pH values lower than the IEP, the zeta potential is positive, reaching 40 mV in the pH range of 2–4 whereas at pH above the IEP, the zeta potential is negative, reaching –40 mV at a pH of 11. This result is consistent with measurements reported by other researchers.<sup>32,33</sup>

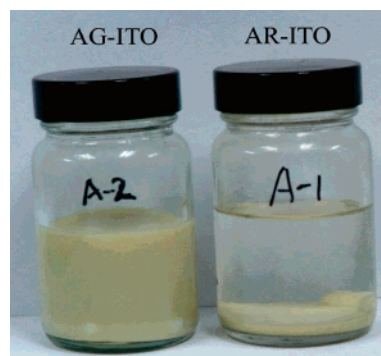
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**Figure 3.** Zeta potential of ITO particles with and without a silica coating.



**Figure 4.** ITO dispersions (0.5 wt %) in 50:50 water/ethanol mixtures. Powders were redispersed in the mixture by sonication for 5 min. The photograph was taken after allowing them to stand for several hours. The appearance of the AG-ITO sample did not change significantly after weeks of standing, with only a small amount of powder found to have precipitated onto the bottom of the bottle.

The pH dependence of the zeta potential for AR-ITO shifted slightly after the first aminosilane treatment step (A-ITO). After the sonogel coating (AG-ITO) in the second step, a more significant shift is observed because of the presence of the silica coating. The IEP also changed to about pH 4, which is close to that of colloidal silica.<sup>34</sup>

To demonstrate the relative dispersability of nanoparticles before and after surface coating, the same amount of each powder sample was dispersed under ultrasound agitation for 5 min in a 50:50 water/ethanol mixture and then left to stand for a period of time. A photograph of the samples is shown in Figure 4, which clearly shows that the dispersion of AG-ITO is much more stable than the AR-ITO powder that was not treated. This change is due to the modified particle surface through the sonogel silica coating; meanwhile, the cavitation effect fragmented the large aggregates into smaller ones or primary particles that promote the dispersability of nanoparticles.

**Reaction Mechanism.** In the first step, the particle surface is modified by a bifunctional organosilane molecule, containing NH– and methoxy groups, to promote subsequent silica coverage. Hydrolysis of the methoxy groups produces silanols (Si–OH), which form covalent bonds with OH groups on the particle surfaces, generating particles with NH-terminated groups attached. Nanolayer coatings can then be attached through the grafted NH groups. In the sonogel coating step, GPTS is first

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hydrolyzed under acidic conditions and power ultrasound irradiation. Large amounts of silanol with attached epoxy groups are generated within a short time, whereas the lack of ethanol in the dispersion inhibits the re-esterification of the silane. Epoxysilanol reacts with grafted aminosilanol on the particle surface by a ring-opening and condensation reaction. Alcohol groups produced by this reaction can then react with epoxy groups to form ether groups, thus binding other hydrolyzed epoxysilanols near the particle surface. Furthermore, the presence of particles in the dispersion enhances cavitation because they act as nucleation sites. This also promotes silica condensation near the particle surface. Through this mechanism a layer of organo-modified silica will assemble to eventually cover the particle surface. The conditions, described in the Experimental Section,

have also been found to be suitable for generating uniform, thin coatings of silica on nanoparticles of other materials such as TiO<sub>2</sub>.

### Summary

We have demonstrated that a two-step sonogel process can be used to treat redispersed nanopowders to generate a thin layer of silica coated on the particle surface. The application of power ultrasound fulfills two functions: it initiates and sustains reactions leading to the growth of silica and disperses the nanoparticles in solution. As a result, the coated powders were more stable when dispersed in aqueous media. This process offers an alternative route for coating nanopowders used in various technological applications.

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